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Research of the Technology of Joint Processing of Stale Copper-Smelting Slags and Pyrite Cinders with the Extraction of Non-Ferrous Metals into a Commercial Product

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Abstract The article deals with the problems of slags processing from copper-smelting production, both current production and those which had been accumulating over many years of enterprises` activity in heaps (stale). There are data about possible methods of slag processing. It is proposed a technology for the joint processing of stale copper-smelting slags of the Urals and pyrite cinders (waste from the production of sulfuric acid) - smelting with obtain a poor matte, into which copper and precious metals will be transferred. The results of scientific research on matte melting are presented. It is shown that when the ratio in the furnace charge "stale slag: pyrite cinder" at the level of 2.5, the extraction of non-ferrous metals into the matte is at the level of 90%.

1. Introduction

Traditionally, the main method of copper production is pyrometallurgical technology[1-6], which includes operations of smelting sulphide concentrates on matte, converting, fire and electrolytic refining. All pyrometallurgical operations are characterized by the formation of a large amount of slag[7-15]. At present, almost all produced slags are processed - refining slags are circulating, and smelting and converter slags are depleted by flotation with obtain a slag concentrate. The widespread introduction of autogenous processes (Vanyukov smelting, Ausmelt process) is accompanied by the obtain of smelting slags with a copper content of 1.5-2%. The need of the process of such slags is primarily due to the fact that the copper content in them often exceeds the copper content in mined ores.

But if slags of the current production are actively processed, then the problem of stale slags remains very urgent. For many decades of operation of copper smelters a huge amount of slag has been accumulated. According to various estimates the amount of stale copper-smelting slags only in the Ural region is about 100-120 million tons. These slag heaps occupy significant areas, but the most important thing is that the average copper content in stale slag is about 1.5-2%, which is higher than the copper content in the currently mined ordinary ores (0.7-1%). This is due to the fact that during the accumulation of slag heaps rich ores were processed, the technologies were imperfect and there were no ways to deplete the slag effectively. In addition to copper old slags contain on average 3% zinc, as well as gold (about 1 g / t) and silver (about 10 g / t)[16].

At present various slag processing technologies are used in the world practice - pyrometallurgical, hydrometallurgical, flotation, combined. The choice of a particular processing method is influenced by the composition of the slag, energy consumption, requirements for processed products, etc. But the processing of stale slag is not always possible or effective with using a technology suitable for slag of current production. In decades of being in heaps slags become compressed, exposed to precipitation, natural oxidants and erosion. All this leads to a changing in the composition of the slags. And the choice of technology for their processing is a difficult task. The main criterion for the efficiency of the technology of stale slags` processing is the extraction of copper from them.

Hydrometallurgical methods of slag processing are based on the transfer of copper into a solution[17-22], and then its separation from the solution in one way or another. Before leaching the slag should be subjected to crushing and grinding that is very costly - slags, especially stale, is a very hard material, their hardness is higher than the hardness of copper ores. In addition, hydrometallurgy makes it possible to transfer oxidized copper compounds into solution well but it`s necessary to convert sulfide and metallic copper into soluble compounds. This can be done only after the first subjecting the slags to such operations as sulfurization, chlorination, etc., which requires additional costs.

After leaching the solutions contain about 1-2 g / l of copper, but up to 40 g / l of iron which makes it difficult to separate copper. And the presence of large amounts of SiO_2 (about 40%) in slags often leads to difficulties in filtering the obtained slurries. Noble metals do not pass into solution. A large volume of slag leads to the production of a large volume of solutions, circulating and rinsing waters that require cleaning. All these problems lead to the limited using of hydrometallurgical methods mainly in the form of semi-industrial and pilot plants.

Now the main method for processing current slags is flotation[22-25]. This method is well mastered, it allows to obtain slag concentrate, use standard equipment and reagents and extract additional precious metals. But flotation is effective when all copper compounds are well opened up, that requires fine grinding - not less than 80-85% of the -0.074-micron fraction. Crushing and grinding stale slag is very costly. In addition, copper in slags exists both in sulfide - easily floatable compounds and in oxidized ones, the flotation of which is difficult. Even the processing of current slags does not allow to obtain copper extraction into concentrate above 70-75%, and during the processing old slags where copper compounds are oxidized under the influence of natural factors, this indicator is even lower - at the level of 60%.

In our opinion, the most promising method for processing stale slag is the pyrometallurgical method. A lot of pyrometallurgical methods have been developed - electrothermal, sulfiding, reducing, reducing-sulfiding, etc. But when choosing a pyrometallurgical technology our purpose was to involve in processing not only stale copper smelting slag but another type of waste - pyrite cinders. This waste was generated during the production of sulfuric acid; a large amount of such waste has been accumulated on the territory of the Sverdlovsk region - more than 4 million tons. Initially they were a finely dispersed material that underwent natural caking during storage. It`s an interesting fact that they contains copper (average content about 0.5%), gold (average content 2 g / t) and silver (average content 25 g / t). The content of sulfur in cinders (2.5 %) is a positive factor for pyrometallurgical technology.

2. Research methods

As objects of research we chose stale slag and pyrite cinders, samples of which were taken at a slag storage and a heaps located in the Sverdlovsk region. The starting materials were analyzed for the content of the main components. The composition of raw materials is presented in table 1.

Table 1. Raw materials composition.

Material	Content (%)									Content (g/t)	
	Cu	Zn	S	Pb	Fe	SiO_2	Al_2O_3	CaO	other	Au	Ag
Stale slag	1.52	3.7	0.78	0.31	28.4	30.3	2.9	9.3	22.79	0.2	9.1
Pyrite cinders	0.31	0.72	3.38	-	52.3	10.2	0.32	-	32.77	0.9	21

The purpose of the experiments is to select a furnace charge for smelting in such way that it would be possible to transfer copper and precious metals to matte and to obtain secondary slags depleted in copper and precious metals which can be used, for example, for the production of building materials.

To obtain mattes it is necessary to convert the oxidized copper into sulfide. This requires sulfur introduced by pyrite cinder:

$$2CuO+2FeS+SiO_2=Cu_2S+2FeO*SiO_2+ SO_2(\uparrow)$$

The main vary parameter was the ratio of pyrite cinder to slag. The main response was the extraction of copper and precious metals into the matte phase.

During the melting of the experimental furnace charge it was necessary to adjust the composition of the secondary slags formed during the melting because an increase in the magnetite content increases the loss of copper with slag. The same result is caused by a lack of silica in the slag. Silica was already present in the starting materials; therefore quartz flux was added only in some of the experimental heats. However, limestone was used as a flux in all experiments because an increase of the CaO content in the slag reduces the loss of copper with secondary slag.

All materials were crushed to a size of -0.1 mm. After weighing the furnace charge was thoroughly mixed. Smelting was carried out in an induction crucible furnace at a temperature of 1300 ˚C. The resulting melt was left in a crucible for maximum settling of the matte and slag phases. After complete cooling of the melt the crucible was broken, matte was separated from the slag, weighed and there was the analysis of the resulting materials. A sample of the resulting cooled matte is shown on Figure 1.

Figure 1. Experimental smelting matte.

3. Results and discussion

The dependences of the extraction of copper and precious metals in matte are based on the results of the data obtained. Tests results are presented on Figure 2.

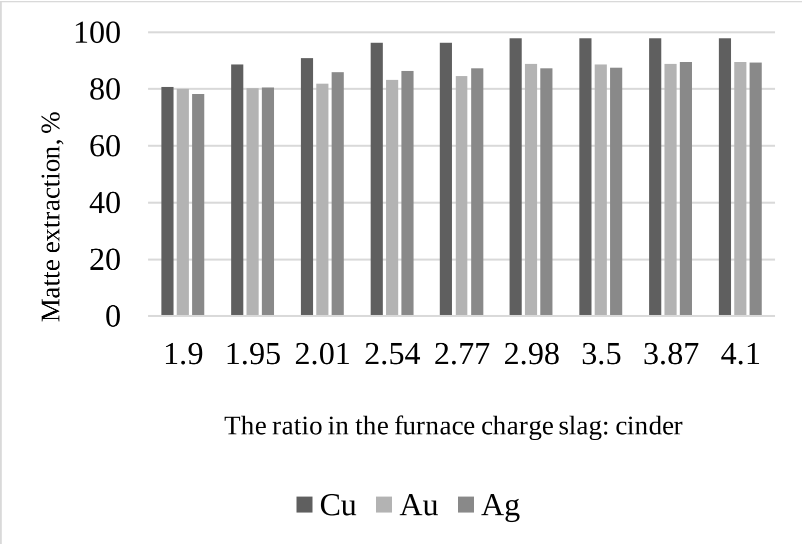

Figure 2. Extraction of copper, gold and silver into matte in dependence on the ratio of stale slag and pyrite cinder in the furnace charge.

Based on the report it can be assumed that the optimum ratio of "slag: cinder" is 2.5. This ratio will allow to convert more than 90% of copper and precious metals into matte. But for a complete assessment of the effect of adding pyrite cinder to the furnace charge it is necessary to assess the yield of secondary slag and the content of metals in it. Tests results are presented on Figure 3, 4.

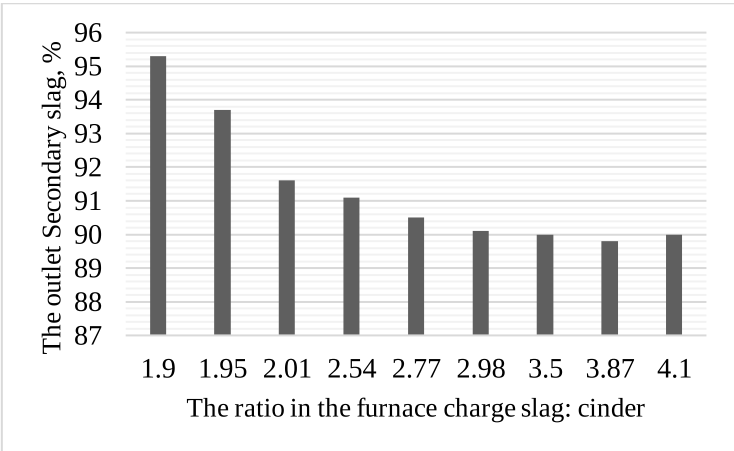

Figure 3. The output of secondary slag depending on the ratio in the charge of stale slag and pyrite cinder.

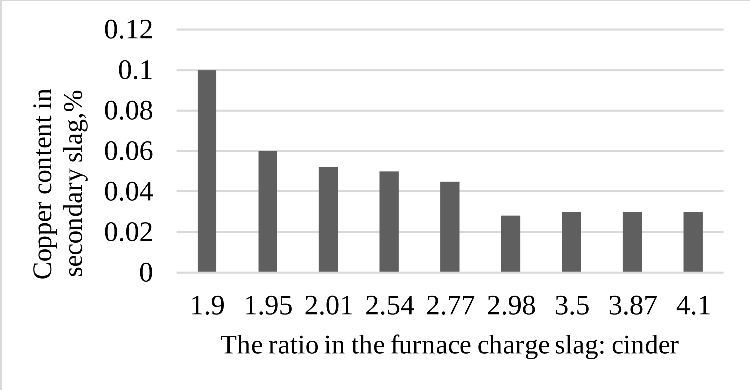

Figure 4. Dependence of the copper content in the secondary slag on the ratio of stale slag and pyrite cinder in the furnace charge.

An increase in the proportion of pyrite cinders in the furnace charge leads to an increase in the yield of secondary slag as slagging of iron, which is part of the cinder, requires the introduction of an additional amount of quartz flux. Without the addition of quartz flux the content of magnetite in the secondary slag increases, which leads to an increase in the loss of copper and precious metals. The low content of noble metals in the secondary slag did not allow to analyze the material correctly. Therefore, for comparison it was selected only the extraction of metals into the matte phase.

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